

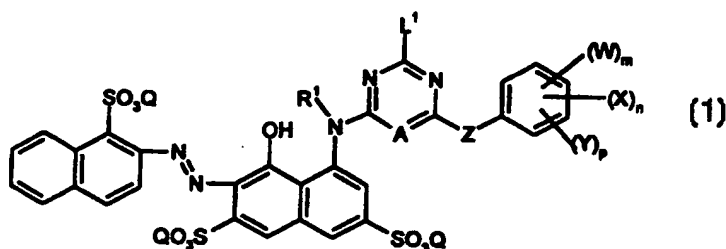
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C09B 43/16, C09D 11/02, D06P 5/00 // C09B 62/245		A1	(11) International Publication Number: WO 99/01510
			(43) International Publication Date: 14 January 1999 (14.01.99)
(21) International Application Number: PCT/GB98/01853		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 24 June 1998 (24.06.98)		Published <i>With international search report.</i>	
(30) Priority Data: 9714010.7 3 July 1997 (03.07.97) GB 9723007.2 1 November 1997 (01.11.97) GB			
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(54) Title: MONOAZO DYES AND INKS CONTAINING THEM

(57) Abstract

Compounds of Formula (1) wherein: A is N, C-Cl, C-CN or C-NO₂; L¹ is -OR³; Z is -O-, -S- or -NR²-; R¹ and R² are each independently H or optionally substituted alkyl; R³ is H or alkyl; each W independently is -CO₂Q or -SO₃Q; each X independently is an optionally substituted amino group or a group which is substituted by an optionally substituted amino group; each Y independently is a substituent other than those defined for W and X; each Q independently is ammonium or substituted ammonium; and m, n and p are as defined in the description. Also claimed are inks containing a compound of Formula (1), an ink jet printing process using the inks, cartridges and a substrate printed with the inks.



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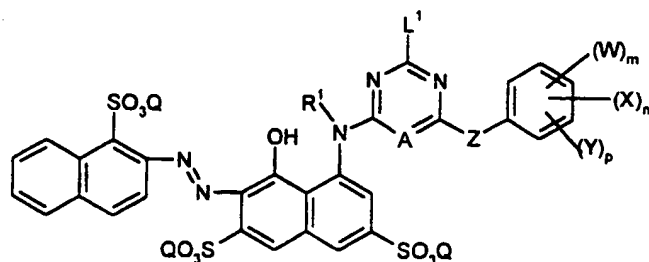
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MONOAZO DYES AND INKS CONTAINING THEM

This invention relates to dyes, to inks and to their use in ink jet printing ("IJP"). IJP is a non-impact printing technique in which droplets of ink are ejected through a fine nozzle onto a substrate without bringing the nozzle into contact with the substrate.

There are many demanding performance requirements for dyes and inks used in IJP. For example they desirably provide sharp, non-feathered images having good water-fastness, light-fastness and optical density. The inks are often required to dry quickly when applied to a substrate to prevent smudging, but they should not form a crust over the tip of an ink jet nozzle because this will stop the printer from working. The inks should also be stable to storage over time without decomposing or forming a precipitate which could block the fine nozzle.

According to a first aspect of the present invention there is provided a compound of Formula (1):



Formula (1)

wherein:

A is N, C-Cl, C-CN or C-NO₂;

L¹ is -OR³;

Z is -O-, -S- or -NR²-;

R¹ and R² are each independently H or optionally substituted alkyl;

R³ is H or alkyl;

each W independently is -CO₂Q or -SO₃Q;

each X independently is an optionally substituted amino group or a group which is substituted by an optionally substituted amino group;

each Y independently is a substituent other than those defined for W and X;

each Q independently is ammonium or substituted ammonium;

m, n and p each independently have a value of from 0 to 3; and (m+n+p) has a value of from 0 to 5.

Preferably A is N.

Preferably m, n and p each independently have a value of 0 or 1.

Preferably n is 1 when m is 0

Preferably (m+n+p) has a value of 1, 2 or 3, more preferably 1 or 2.

Z is preferably -NR²-, more preferably -NH-.

Preferably each Y independently is halo, more preferably F or Cl; hydroxy; nitro; cyano; optionally substituted alkyl, preferably optionally substituted C₁₋₁₀-alkyl, especially C₁₋₄-alkyl; optionally substituted alkoxy, preferably optionally substituted C₁₋₁₀-alkoxy, more preferably C₁₋₄-alkoxy; optionally substituted aryl, preferably optionally substituted phenyl or optionally substituted naphthyl; optionally substituted aralkyl, preferably optionally substituted C₇₋₁₂-aralkyl, more preferably phenyl-(C₁₋₆-alkylene)-, especially phenyl-CH₂-; -SR^a; -COR^a; -COOR^a; -SO₃R^a; -SO₂R^a; or -SOR^a; wherein R^a is optionally substituted C₁₋₄-alkyl; wherein the optional substituents are selected from carboxy, sulpho, hydroxy, nitro, cyano and halo.

R¹ and R² are preferably each independently H or optionally substituted C₁₋₄-alkyl, more preferably H, C₁₋₄-alkyl or C₂₋₄-alkyl substituted by hydroxy, carboxy, sulpho or cyano. Examples include methyl, ethyl, n-propyl, iso-propyl, hydroxyethyl, cyanoethyl, sulphopropyl and carboxyethyl. It is especially preferred that R¹ and R² are H.

Preferably the compounds of Formula (1) are monoazo compounds (i.e. they contain only one azo (-N=N-) group).

R³ is preferably H or C₁₋₁₀-alkyl, more preferably H or C₁₋₆-alkyl, especially H or C₁₋₄-alkyl, more especially H.

When X is, or is substituted by, an optionally substituted amino group, the optionally substituted amino group preferably has a pK_a of from 12 to 4, more preferably of from 10 to 6.

The optionally substituted amino groups referred to in the definition of X are preferably of the formula -NR⁴R⁵ wherein R⁴ and R⁵ are each independently H or optionally substituted alkyl; or R⁴ and R⁵ together with the nitrogen atom to which they are attached form a 5- or 6- membered ring.

When R⁴ or R⁵ is optionally substituted alkyl it is preferably optionally substituted C₁₋₆-alkyl, more preferably optionally substituted C₁₋₄-alkyl. Preferred substituents are selected from carboxy, sulpho, hydroxy, amino and C₁₋₄-alkoxy.

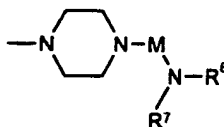
When R⁴ and R⁵ together with the nitrogen to which they are attached form an optionally substituted 5- or 6- membered ring they preferably form optionally substituted morpholine, more preferably optionally substituted piperazine. The substituents are preferably selected from hydroxy, carboxy, sulpho, C₁₋₆-alkoxy, C₁₋₆-alkyl and C₁₋₆-alkyl substituted by hydroxy, carboxy, sulpho or an optionally substituted amino group.

A preferred substituted morpholine or piperazine ring carries a group of the formula -M-NR⁶R⁷ wherein M is an alkylene linking group and R⁶ and R⁷ are each

independently H, C₁₋₆-alkyl or C₁₋₆-alkyl substituted by hydroxy, carboxy, sulpho, amino or C₁₋₄-alkoxy.

M is preferably C₁₋₆-alkylene, more preferably C₂₋₆-alkylene and especially -(CH₂)_g-, where g is from 2 to 6.

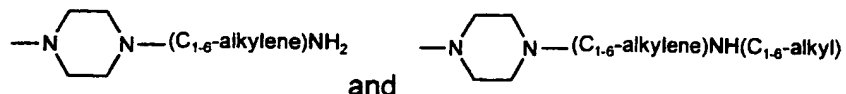
An especially preferred substituted piperaziny group is of the Formula (2):



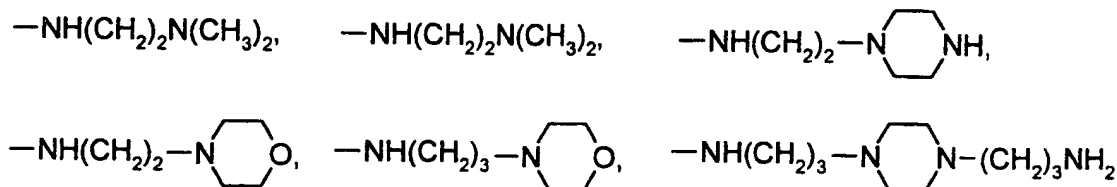
Formula (2)

wherein M, R⁶ and R⁷ are as hereinbefore defined.

Preferred groups of the Formula (2) include



Examples of optionally substituted amino groups include: -NH₂, -NHCH₂CH₃, -N(CH₂CH₃)₂, -NHCH₂CH₂OH:



When X is a group which is substituted by an optionally substituted amino group it preferably comprises optionally interrupted alkylene carrying a -NR⁴R⁵ group wherein R⁴ and R⁵ are as hereinbefore defined.

Preferably the optionally interrupted alkylene group comprise one, two or three C₂₋₁₀-alkylene chains and 0, 1, 2, 3 or 4 interrupting groups selected from O, CO, CO₂, S, SO, SO₂, NH, optionally substituted phenylene, CONH and SO₂NH. The interrupting groups may link each of the C₂₋₁₀-alkylene chains and/or be at a terminal position in the interrupted alkylene chain.

Preferred interrupted alkylene groups having one C₂₋₁₀-alkylene chain and one interrupting group are of the formula -SO₂NH-(C₂₋₁₀-alkylene)-; -NHCO₂-(C₂₋₁₀-alkylene)-; -CONH-(C₂₋₁₀-alkylene)-; -NHCO-(C₂₋₁₀-alkylene)-; -[(O, S or NH)-C₂₋₁₀-alkylene]-; -SO-(C₂₋₁₀-alkylene)-; and -SO₂-(C₂₋₁₀-alkylene)-.

Preferred interrupted alkylene groups having two C_{2-10} -alkylene chains and two interrupting groups are any two of the groups described in the previous paragraph attached together, especially $-SO_2-(C_{2-10}\text{-alkylene})-NH-(C_{2-10}\text{-alkylene})-$.

Q is preferably of the formula *NT_4 wherein each T independently is H or optionally substituted alkyl, or two groups represented by T are H or optionally substituted alkyl and the remaining two groups represented by T, together with the N atom to which they are attached, form a 5- or 6- membered ring (preferably a morpholine, pyridine or piperidine ring).

Preferably each T independently is H or C_{1-4} -alkyl, more preferably H, CH_3 or CH_3CH_2 , especially H. Thus Q is preferably ammonium (i.e. *NH_4).

Examples of groups represented by Q include *NH_4 , morpholinium, piperidinium, pyridinium, $(CH_3)_3N^+H$, $(CH_3)_2N^+H_2$, $H_2N^+(CH_3)(CH_2CH_3)$, $CH_3N^+H_3$, $CH_3CH_2N^+H_3$, $H_2N^+(CH_2CH_3)_2$, $CH_3CH_2CH_2N^+H_3$, $CH_3CH_2CH_2N^+H_3$, $(CH_3)_2CHN^+H_3$, $N^+(CH_3)_4$, $N^+(CH_2CH_3)_4$, N-methyl pyridinium, N,N-dimethyl piperidinium and N,N-dimethyl morpholinium.

A first preferred embodiment of the present invention comprises a compound of the Formula (1) and salts thereof wherein:

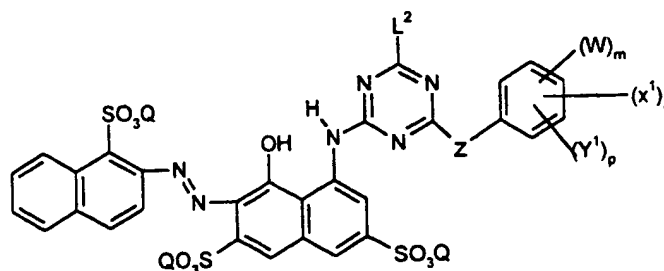
- A is N;
 m is 0, 1 or 2;
 n is 0 or 1;
 p is 0 or 1;
 X is of the formula $-NR^4R^5$ or a group which is substituted by $-NR^4R^5$;
 Y is halo, hydroxy, cyano, C_{1-4} -alkyl, C_{1-4} -alkoxy, $-SR^a$, $-COR^a$, $-COOR^a$, $-SO_3R^a$, $-SO_2R^a$ or $-SOR^a$; and

R^1 , R^2 , R^3 , R^4 , R^5 , R^a , Q and W are as hereinbefore defined.

In the first preferred embodiment it is especially preferred that Y is C_{1-4} -alkyl.

A second preferred embodiment comprises a monoazo compound of the Formula

(3):



Formula (3)

wherein:

Z

is $-O-$, $-S-$ or $-NR^b-$;

R^8 is H or C_{1-4} -alkyl optionally substituted by hydroxy, carboxy, sulpho or cyano;
 L^2 is $-OR^8$;
 R^9 is H or C_{1-4} -alkyl;
 5 each W independently is $-CO_2Q$ or $-SO_3Q$;
 each X^1 is $-NR^4R^5$, $-SO_2-NR^4R^5$, $-SO_2(C_{1-10}\text{-alkylene})-NR^4R^5$ or C_{1-6} -alkyl substituted by $-NR^4R^5$;
 each Y^1 independently is Cl, nitro, cyano, C_{1-10} -alkyl, or C_{1-10} -alkyl substituted by hydroxy, carboxy, sulpho, or C_{1-6} -alkoxy;
 10 m, n and p are each independently 0 or 1;
 (m+n+p) is 1, 2 or 3; and
 Q , R^4 and R^5 are as hereinbefore defined;
 provided that n is 1 when m is 0.

15 In preferred compounds of Formula (3) R^4 and R^5 are each independently H or optionally substituted C_{1-6} -alkyl as hereinbefore described, or $-NR^4R^5$ is of Formula (2) as hereinbefore defined.

Preferred compounds in the second embodiment comprise a compound of Formula (3) as hereinbefore defined wherein:

Z is $-NR^8$;

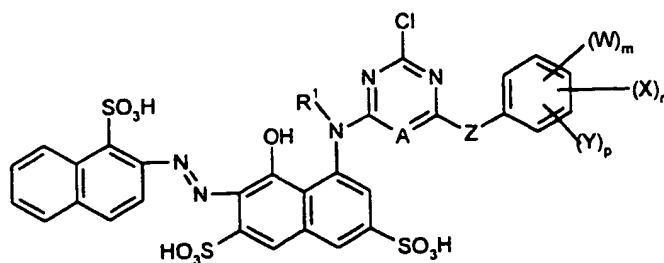
20 Y^1 is C_{1-6} -alkyl;

L^2 is $-OH$ or methoxy; and

R^8 , W, X^1 , m, n, p, R^4 and R^5 are as hereinbefore defined, provided that n is 1 when m is 0.

25 The compounds of Formula (1) and (3) may be made from corresponding compounds in the free acid or alkali metal salt form using techniques known in the art. For example, an alkali metal salt of a dye may be converted into a salt with ammonia or an amine by dissolving an alkali metal salt of the dye in water, acidifying with a mineral acid and adjusting the pH of the solution to pH 9 to 9.5 with ammonia or the amine and removing the alkali metal cations by dialysis.

30 The compounds may be prepared in the free acid or salt form using conventional techniques for the preparation of azo dyes. For example a suitable method comprises condensing a compound of the Formula (4) with a compound of the Formula L^1H :



Formula (4)

wherein:

R¹, Z, A, W, X, Y, m, n, p are as hereinbefore defined.

The condensation is preferably performed in a liquid medium, more preferably an aqueous medium and especially water. Temperatures of 15°C to 100°C are preferred, more preferably from 60 to 90°C. Preferably a reaction time of 1 to 48, more preferably 3 to 24 hours is used.

The condensation is preferably performed in the presence of a base. The base may be any inorganic base for example, ammonia, an alkali metal or alkali earth metal hydroxide, carbonate or bicarbonate, or an organic base. Preferred organic bases are tertiary amines for example, N-alkylated heterocycles, for example N-(C₁-₄-alkyl)morpholine, N-(C₁-₄-alkyl)piperidine, N,N'-di(C₁-₄-alkyl)piperazine; tri(C₁-₄-alkyl)amines, for example triethylamine, and optionally substituted pyridines, especially pyridine.

The amount of base used may be varied between wide limits but it is preferred to use less than 40, more preferably less than 10 and especially from 3 to 5 moles for each mole of the compound of Formula (4).

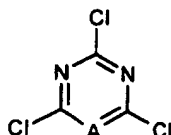
After the condensation the product may be isolated by precipitating the product as a salt from the reaction mixture for example by the addition of a suitable alkali metal salt, especially sodium chloride. Alternatively, the product may be isolated in its free acid form by acidifying the reaction mixture, preferably using a mineral acid, especially hydrochloric acid. Where the product precipitates as a solid it may be separated from the mixture by filtration.

If desired unwanted anions may be removed from the product of the above process by dialysis, osmosis, ultrafiltration or a combination thereof.

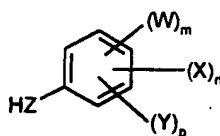
The product of the above process may be converted to the ammonium or substituted ammonium salt by the addition of ammonia, ammonium hydroxide, primary, secondary, tertiary or quaternary amine. When the base used in the condensation process is an organic amine an excess may be used so that the compound of Formula (1) is formed as the substituted ammonium salt.

The compound of the Formula (4) may be prepared using conventional techniques, for example by:

- (1) diazotising 2-naphthylamine-1-sulphonic acid to give the corresponding diazonium salt;
- (2) coupling the diazonium salt from stage (1) with 1-acetamido-8-naphthol-3,6-disulphonic acid at a pH > 7, preferably at a pH of from 8 to 9;
- (3) alkaline hydrolysis of the product of stage (2) to remove the acetyl group;
- (4) condensing the product from stage (1) with a compound of the formula:



- wherein A is as hereinbefore defined; and
- (5) condensing the product from stage (4) with approximately 1 molar equivalent of the compound of the formula:



wherein Z, W, X, Y, m, n and p are as hereinbefore defined.

The diazotisation in stage (1) is preferably performed in an aqueous medium at a pH below 7 in the presence of a suitable diazotisation agent. Dilute mineral acid, e.g. HCl or H₂SO₄, is preferably used to achieve the desired acidic conditions. Conveniently the diazotisation agent is formed in-situ, for example by dissolving an alkali metal nitrite, preferably sodium nitrite, in a molar excess of mineral acid, preferably HCl. Normally at least one mole of diazotisation agent per mole of 2-naphthylamine-1-sulphonic acid, preferably from 1 to 1.25 moles will be used in the diazotisation.

The temperature of the diazotisation is not critical and may conveniently be carried out at from -5°C to 20°C, preferably from 0 to 10°C and especially from 0 to 5°C.

The hydrolysis in stage (3) is preferably performed at a pH in the range 9 to 14. The temperature during hydrolysis is preferably from 40 to 90°C.

According to a second aspect of the present invention there is provided an ink comprising:

- (a) from 0.01 to 30 parts of a compound of the Formula (1), or preferably of Formula (3), as hereinbefore defined except that Q is any cation; and
- (b) from 70 to 99.99 parts of a medium comprising component (i), (ii) or (iii):
 - (i) a mixture of water and an organic solvent;
 - (ii) an organic solvent free from water; or
 - (iii) a low melting point solid;

wherein all parts are by weight and the number of parts of (a)+(b)=100.

In preferred compounds which may be used in the component (a) of the ink Q is H or an alkali metal, more preferably Q is sodium, ammonium or substituted ammonium. It is especially preferred that Q is ammonium or substituted ammonium as hereinbefore defined in the first aspect of the present invention.

The number of parts of component (a) is preferably from 0.1 to 20, more preferably from 0.5 to 15, and especially from 1 to 5 parts. The number of parts of component (b) is preferably from 99.9 to 80, more preferably from 99.5 to 85, especially from 99 to 95 parts.

When the medium is a mixture of water and an organic solvent or an organic solvent free from water, preferably component (a) is completely dissolved in component (b). Preferably component (a) has a solubility in component (b) at 20°C of at least 10%. This allows the preparation of concentrates which may be used to prepare more dilute inks and reduces the chance of the dye precipitating if evaporation of the liquid medium occurs during storage.

When the medium comprises a mixture of water and an organic solvent, the weight ratio of water to organic solvent is preferably from 99:1 to 1:99, more preferably from 99:1 to 50:50 and especially from 95:5 to 80:20.

It is preferred that the organic solvent present in the mixture of water and organic solvent is a water-miscible organic solvent or a mixture of such solvents. Preferred water-miscible organic solvents include C₁₋₆-alkanols, preferably methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol, n-pentanol, cyclopentanol and cyclohexanol; linear amides, preferably dimethylformamide or dimethylacetamide; ketones and ketone-alcohols, preferably acetone, methyl ether ketone, cyclohexanone and diacetone alcohol; water-miscible ethers, preferably tetrahydrofuran and dioxane; diols, preferably diols having from 2 to 12 carbon atoms, for example pentane-1,5-diol, ethylene glycol, propylene glycol, butylene glycol, pentylene glycol, hexylene glycol and thiodiglycol and oligo- and poly-alkyleneglycols, preferably diethylene glycol, triethylene glycol, polyethylene glycol and polypropylene glycol; triols, preferably glycerol and 1,2,6-hexanetriol; mono-C₁₋₄-alkyl ethers of diols, preferably mono-C₁₋₄-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)-ethanol, 2-[2-(2-methoxyethoxy)ethoxy]ethanol, 2-[2-(2-ethoxyethoxy)-ethoxy]-ethanol and ethyleneglycol monoallylether; cyclic amides, preferably 2-pyrrolidone, N-methyl-2-pyrrolidone, N-ethyl-2-pyrrolidone, caprolactam and 1,3-dimethylimidazolidone; cyclic esters, preferably caprolactone; sulphoxides, preferably dimethyl sulphoxide and sulpholane. Preferably the liquid medium comprises water and 2 or more, especially from 2 to 8, water-soluble organic solvents.

Especially preferred water-miscible organic solvents are cyclic amides, especially 2-pyrrolidone, N-methyl-pyrrolidone and N-ethyl-pyrrolidone; diols, especially 1,5-pentane diol, ethyleneglycol, thiodiglycol, diethyleneglycol and triethyleneglycol; and mono- C₁₋₄-alkyl and

C₁₋₄-alkyl ethers of diols, more preferably mono- C₁₋₄-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxy-2-ethoxy-2-ethoxyethanol.

A preferred medium comprises:

- (a) from 75 to 95 parts water; and
- (b) from 25 to 5 parts in total of one or more solvents selected from diethylene glycol, 2-pyrrolidone, thiodiglycol, N-methylpyrrolidone, cyclohexanol, caprolactone, caprolactam and pentane-1,5-diol;

wherein the parts are by weight and the sum of the parts (a) and (b) = 100.

Examples of further suitable ink media comprising a mixture of water and one or more organic solvents are described in US 4,963,189, US 4,703,113, US 4,626,284 and EP 4,251,50A.

When the liquid medium comprises an organic solvent free from water, (i.e. less than 1% water by weight) the solvent preferably has a boiling point of from 30° to 200°C, more preferably of from 40° to 150°C, especially from 50 to 125°C. The organic solvent may be water-immiscible, water-miscible or a mixture of such solvents. Preferred water-miscible organic solvents are any of the hereinbefore described water-miscible organic solvents and mixtures thereof. Preferred water-immiscible solvents include, for example, aliphatic hydrocarbons; esters, preferably ethyl acetate; chlorinated hydrocarbons, preferably CH₂Cl₂; and ethers, preferably diethyl ether; and mixtures thereof.

When the liquid medium comprises a water-immiscible organic solvent, preferably a polar solvent is included because this enhances solubility of the dye in the liquid medium. Examples of polar solvents include C₁₋₄-alcohols. In view of the foregoing preferences it is especially preferred that where the liquid medium is an organic solvent free from water it comprises a ketone (especially methyl ethyl ketone) &/or an alcohol (especially a C₁₋₄-alkanol, more especially ethanol or propanol).

The organic solvent free from water may be a single organic solvent or a mixture of two or more organic solvents. It is preferred that when the medium is an organic solvent free from water it is a mixture of 2 to 5 different organic solvents. This allows a medium to be selected which gives good control over the drying characteristics and storage stability of the ink.

Ink media comprising an organic solvent free from water are particularly useful where fast drying times are required and particularly when printing onto hydrophobic and non-absorbent substrates, for example plastics, metal and glass.

Preferred low melting solid media have a melting point in the range from 60°C to 125°C. Suitable low melting point solids include long chain fatty acids or alcohols, preferably those with C₁₈₋₂₄ chains, and sulphonamides. The dye of Formula (1) or (3) may be dissolved in the low melting point solid or may be finely dispersed in it.

The dyes according to the present invention exhibit a high solubility in aqueous media, accordingly it is preferred that the liquid medium is a mixture of water and one or more water miscible organic solvent(s).

The ink may also contain additional components conventionally used in ink jet printing inks, for example viscosity and surface tension modifiers, pH buffers (e.g. 1:9 citric acid/sodium citrate) corrosion inhibitors, biocides, kogation reducing additives and surfactants which may be ionic or non-ionic.

The presence of impurities in an ink jet printing ink can result in the formation of precipitates in the ink. This is undesirable because the precipitates can block the narrow ink jet nozzle in the printer. Therefore, the dye(s) according to the present invention may be, and preferably are, purified to remove undesirable impurities before they are incorporated into inks for ink jet printing. Conventional techniques may be employed for purifying the dyes, for example osmosis and / or dialysis.

A third aspect of the present invention provides a process for printing an image on a substrate comprising applying an ink according to the second aspect of the present invention to the substrate by means of an ink jet printer.

Preferred inks used in this process contain a dye of the Formula (1) or Formula (3) are as defined in the first aspect of the present invention.

The ink jet printer preferably applies the ink to the substrate in the form of droplets which are ejected through a small orifice onto the substrate. Preferred ink jet printers are piezoelectric ink jet printers and thermal ink jet printers. In thermal ink jet printers, programmed pulses of heat are applied to the ink in a reservoir by means of a resistor adjacent to the orifice, thereby causing the ink to be ejected in the form of small droplets directed towards the substrate during relative movement between the substrate and the orifice. In piezoelectric ink jet printers the oscillation of a small crystal causes ejection of the ink from the orifice.

The substrate is preferably paper, plastic, a textile, metal or glass, more preferably paper, an overhead projector slide or a textile material, especially paper.

Preferred papers are plain or treated papers which may have an acid, alkaline or neutral character. Examples of commercially available papers include, HP Premium Coated Paper, HP Photopaper (all available from Hewlett Packard Inc), Stylus Pro 720 dpi Coated Paper, Epson Photo Quality Glossy Film, Epson Photo Quality Glossy Paper (available from Seiko Epson Corp.), Canon HR 101 High Resolution Paper, Canon GP 201 Glossy Paper, Canon HG 101 High Gloss Film (all available from Canon Inc.), Wiggins Conqueror paper (available from Wiggins Teape Ltd), Xerox Acid Paper and Xerox Alkaline paper, Xerox Acid Paper (available from Xerox).

A fourth aspect of the present invention provides a paper, an overhead projector slide or a textile material printed with an ink according to the second aspect of the present invention, or by means of the process according to the third aspect of the present invention.

When the substrate is a textile material the ink according to the invention is preferably applied thereto by:

- i) applying the ink to the textile material using an ink jet printer; and
- ii) heating the printed textile material at a temperature of from 50°C to 250°C.

Preferred textile materials are natural, synthetic and semi-synthetic materials. Examples of preferred natural textile materials include wool, silk, hair and cellulosic materials, particularly cotton, jute, hemp, flax and linen. Examples of preferred synthetic and semi-synthetic materials include polyamides, polyesters, polyacrylonitriles and polyurethanes.

Preferably the textile material has been treated with an aqueous pre-treatment composition comprising a thickening agent and optionally a water-soluble base and a hydrotropic agent and dried prior to step i) above.

The pre-treatment composition preferably comprises a solution of the base and the hydrotropic agent in water containing the thickening agent. Particularly preferred pre-treatment compositions are described more fully in European Patent Application No.534660A1.

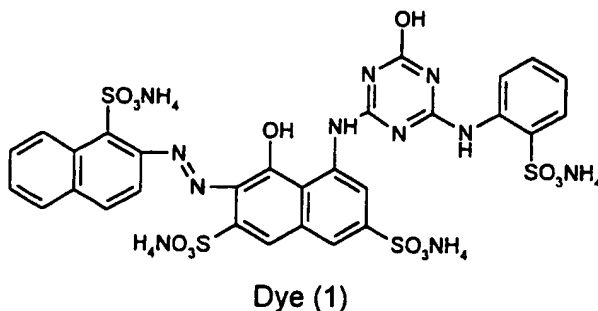
A fifth aspect of the present invention provides an ink jet printer cartridge containing an ink according to the second aspect of the present invention. The ink jet printer cartridge is optionally refillable.

The invention is further illustrated by the following Examples in which all parts and percentages are by weight unless otherwise stated.

Example 1

Dye

Dye (1) was prepared using the method described below:



Stage (i)

2-Naphthylamine-1-sulphonic acid (0.304M, 67.84g at 100%) was added to water (500ml) and cooled to 0-5°C. Concentrated HCl (150ml) was then added followed by 2N NaNO₂ (150ml). The solution was stirred for 1 hour at 0-5°C and excess NaNO₂ was destroyed by addition of sulphamic acid.

To the above solution was added 1-acetamido-8-naphthol-3,6-disulphonic acid (0.304M, 109.83g at 100%) in water (500ml). The pH was then raised to 7.0 by addition of a concentrated solution of NaOH and the solution was stirred for 3 hours at 0-5°C. The solution was then adjusted to 1.5M NaOH by addition of NaOH pellets and was heated to 85°C for 6 hours.

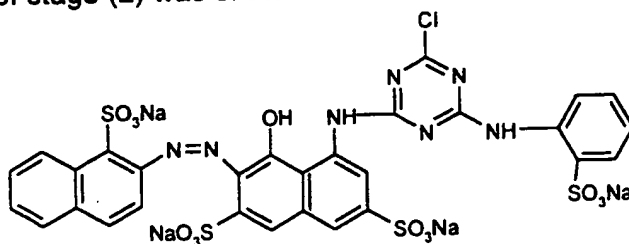
The pH was then reduced to 7.0 by addition of concentrated HCl and the solution was salted to 20% with NaCl. The resulting precipitate was filtered off, washed and dried. Strength estimated at 71.6%.

Stage (ii)

The product of stage (i) above (86.5g, 0.1 mole at 71.6% strength) was dissolved in water (800ml). Cyanuric chloride (19.36g, 0.105 mole) was dissolved in acetone (200ml) and added to ice/water (300g). To this was added the solution of the product of stage (i) allowing the pH to fall. The resulting solution was stirred for 2 hours at 0-5°C. The pH was then raised to 7.0 by addition 2N NaOH solution and the solution was allowed to self-warm to room temperature.

2-Aminobenzenesulphonic acid (0.11 mole, 19.05g) was added to the solution and the pH was maintained at 7 by addition 2N NaOH. The reaction mixture was stirred to 6 hours at room temperature. The solution was then salted to 20% with NaCl. The resulting precipitate was filtered off, washed and dried.

The product of stage (2) was of the formula:

Stage (iii)

The product of stage (ii) above (33g, 0.025 mole at 70% strength) was dissolved in water (300ml) and the pH adjusted to 12.0 by addition of NaOH. The solution was heated to 90°C for 8 hours maintaining pH at 12.0 by addition of 2N NaOH. The pH was then lowered to 7.0 by addition of concentrated HCl and was cooled to room temperature. The solution was salted to 20% w/w with NaCl and the resulting precipitated isolated by filtration.

The solid was purified by dialysis. Finally the purified compound was converted to the ammonium salt by ion exchange solution to give the title product.

Ink

Ink (1) was prepared by dissolving 2 parts of Dye (1) in 98 parts of a mixture comprising 90 parts water and 10 parts 2-pyrrolidone. The pH of the ink was 7.0.

Ink Jet Printing

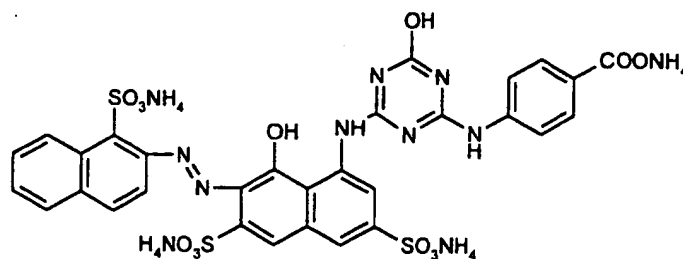
Ink 1 was applied to plain paper using a Hewlett Packard HP 660C ink jet printer, giving prints which were bright magenta in shade.

The optical density of the resulting prints was 1.2 to 1.3, as measured using an X-Rite densitometer.

The prints exhibited an excellent light fastness. After 64 hours exposure in an Atlas Weatherometer the optical density of the prints had only reduced by 10%.

Example 2

Dye (2)



Dye (2)

Dye (2) was prepared as described in Example 1, except that the 2-aminobenzenesulphonic acid used in stage (ii) was replaced with 4-amino benzoic acid.

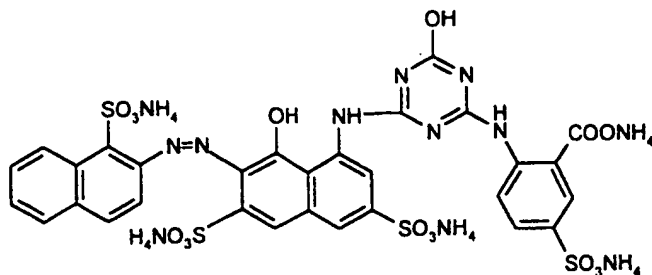
Ink

Ink (2) was prepared by dissolving 2 parts of Dye (2) in 98 parts of a mixture comprising 90 parts water and 10 parts 2-pyrrolidone. The pH of the ink was 7.0.

Ink Jet Printing

Ink (2) was applied to plain paper using an ink jet printer as described in Example 1 giving prints which were bright magenta in shade. The optical density and light fastness of the prints was measured as described in Example 1.

The prints exhibited an excellent light fastness.

Example 3Dye (3)

Dye(3)

Dye (3) was prepared as described in Example 1, except that the 2-aminobenzenesulphonic acid used in stage (ii) was replaced with 2-amino-5-sulphobenzoic acid.

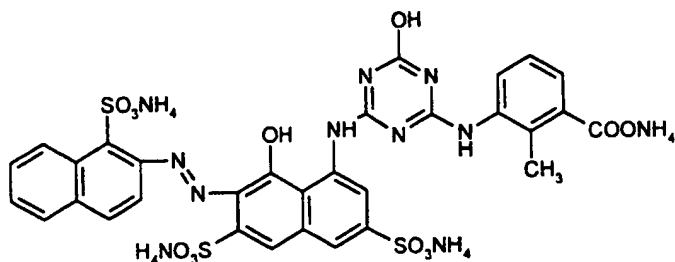
Ink

Ink (3) was prepared by dissolving 2 parts of Dye (3) in 98 parts of a mixture comprising 90 parts water and 10 parts 2-pyrrolidone. The pH of the ink was 7.0.

Ink Jet Printing

Ink (3) was applied to plain paper using an ink jet printer as described in Example 1 giving prints which were bright magenta in shade. The optical density and light fastness of the prints was measured as described in Example 1.

The prints exhibited an excellent light fastness.

Example 4Dye (4)

Dye (4)

Dye (4) was prepared as described in Example 1, except that the 2-aminobenzenesulphonic acid used in stage (ii) was replaced with 3-amino-2-methylbenzoic acid.

Ink

Ink (4) was prepared by dissolving 2 parts of Dye (4) in 98 parts of a mixture comprising 90 parts water and 10 parts 2-pyrrolidone. The pH of the ink was 7.0.

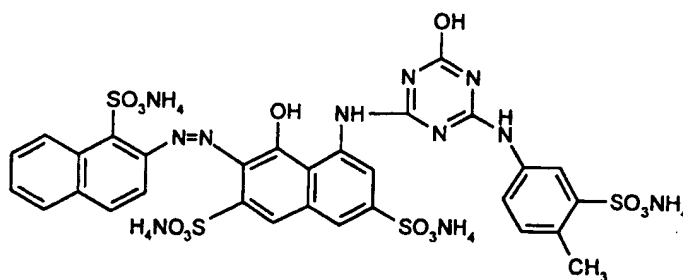
Ink Jet Printing

Ink (4) was applied to plain paper using an ink jet printer as described in Example 1 giving prints which were bright magenta in shade. The optical density and light fastness of the prints was measured as described in Example 1.

The prints exhibited an excellent light fastness.

Example 5

Dye (5)



Dye (5)

Dye (5) was prepared as described in Example 1, except that the 2-aminobenzenesulphonic acid used in stage (ii) was replaced with 5-amino-2-methylbenzenesulphonic acid.

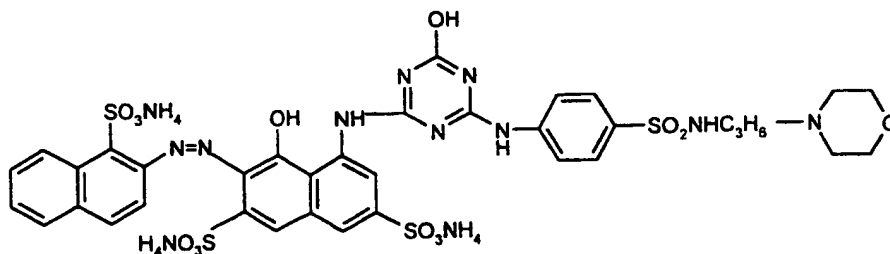
Ink

Ink (5) was prepared by dissolving 2 parts of Dye (5) in 98 parts of a mixture comprising 90 parts water and 10 parts 2-pyrrolidone. The pH of the ink was 7.0.

Ink Jet Printing

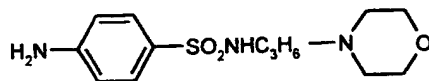
Ink (5) was applied to plain paper using an ink jet printer as described in Example 1 giving prints which were bright magenta in shade. The optical density and light fastness of the prints was measured as described in Example 1.

The prints exhibited an excellent light fastness.

Example 6Dye (6)

Dye (6)

Dye (6) was prepared as described in Example 1, except that that 2-aminobenzene sulphonic acid used in stage (ii) was replaced with Intermediate (1) of the formula:



Intermediate (1)

Intermediate (1) was prepared as follows:

N-Acetylsulfanilyl chloride (116.5g, 0.5 mole) was stirred in water (300ml). To this was added 4-(3-aminopropyl)morpholine (108.15g, 0.75 mole) dropwise over approx. 30 minutes. The reaction mixture was then stirred for 12 hours at room temperature. Concentrated HCl (100ml) was then added and the solution heated to 70°C for 5 hours. The pH was then raised to 7 by the addition of concentrated NaOH and the solution salted to 20% with NaCl. The resulting precipitate was filtered off, washed and dried to leave the title product. Strength estimated at 81.5%.

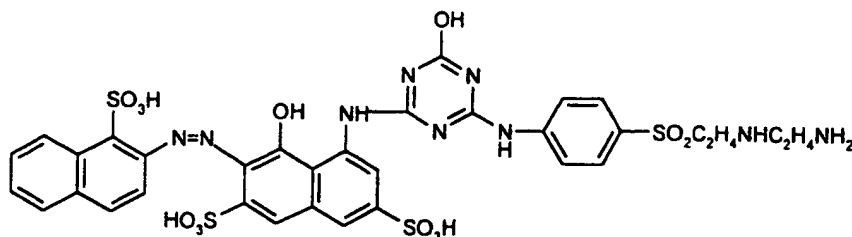
Ink

Ink (6) was prepared by dissolving 2 parts of Dye (6) in 98 parts of a mixture comprising 90 parts water and 10 parts 2-pyrrolidone. The pH of the ink was 7.0.

Ink Jet Printing

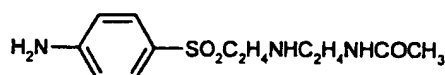
Ink (6) was applied to plain paper using an ink jet printer as described in Example 1 giving prints which were bright magenta in shade. The optical density and light fastness of the prints was measured as described in Example 1.

The prints exhibited an excellent light fastness.

Example 7Dye (7)

Dye (7)

Dye (7) was prepared as described in Example 1, except that the 2-aminobenzene sulphonic acid used in stage (ii) was replaced with Intermediate (2) of the formula:



Intermediate (2)

Intermediate (2) was prepared as follows:

p-Aminobenzenesulphatoethylsulphone (0.14 mole, 39.34g) and N-acetyleneethylenediamine (0.42 mole, 47.7g) were added to water. The resulting mixture was heated to 60 degrees for 4 hours, whilst maintaining the pH at 8.5 by addition of aqueous sodium hydroxide solution. Water was then removed from the mixture by distillation to yield a brown oil which crystallised on standing. The crystalline solid was slurried in a small amount of water, isolated by filtration, washed with ethanol and pulled dry to leave the title product. (Yield = 22.21g)

Ink

Ink (7) was prepared by dissolving 2 parts of Dye (7) in 98 parts of a mixture comprising 90 parts water and 10 parts 2-pyrrolidone. The pH of the ink was 7.0.

Ink Jet Printing

Ink (7) was applied to plain paper using an ink jet printer as described in Example 1 giving prints which were bright magenta in shade. The optical density and light fastness of the prints was measured as described in Example 1.

The prints exhibited an excellent light fastness.

Example 8

The inks described in Tables I and II may be prepared wherein the Dye described in the first column is the Dye made in the above Example of the same number. Numbers quoted in the second column onwards refer to the number of parts of the relevant

ingredient and all parts are by weight. The inks may be applied to paper by thermal or piezo ink jet printing.

The following abbreviations are used in Table I and II:

PG = propylene glycol

NMP = N-methyl pyrrolidone

IPA = isopropanol

2P = 2-pyrrolidone

P12 = propane-1,2-diol

CET = cetyl ammonium bromide

TBT = tertiary butanol

DEG = diethylene glycol

DMK = dimethylketone

MEOH = methanol

MIBK = methylisobutyl ketone

BDL = butane-2,3-diol

PHO = Na_2HPO_4 and

TDG = 1,3-bis(2-hydroxyethyl) urea

TABLE I

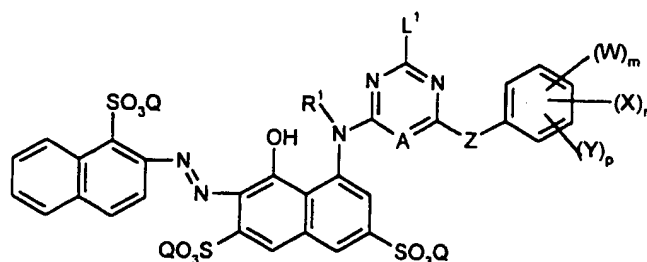
Dye	Dye Content	Water	PG	DEG	NMP	DMK	NaO H	Na Stearate	IPA	MEOH	2P	MIBK
1	2.0	80	5		6	4					5	
2	3.0	90		5	4.8		0.2					
3	10.0	85	3		3	3				5	1	
5	2.1	91		8								1
2	3.1	86	4.8					0.2	4			5
1	1.1	81			9		0.5		6		9	
7	2.5	60	4	15	3	3			10		5	4
6	5	65		20								
4	2.4	75	5	4		5				6		5
6	4.1	80	3	5	2	9.7		0.3				
7	3.2	65		5	4	6			5	4	6	5
3	5.1	96								4		
1	10.8	90	5						5	4		
2	10.0	80	2	6	2	5			1		4	
4	1.8	80		5							15	
3	2.6	84			11						5	
3	3.3	80	2			10				2		6
2	12.0	90				6.7	0.3		3			
5	5.4	69	2	20	2	1					3	3
4	6.0	91			4						5	

TABLE II

Dye	Dye Content	Water	PG	DEG	NMP	CET	TBT	TDG	BDL	PHO	2P	PI2
5	3.0	80	15			0.2				1.2	4.8	3.8
6	9.0	90		5								
5	1.5	85	5	5		0.15	4.65	0.2		0.12		
7	2.5	90		6	3.88							6
1	3.1	82	4	7.7		0.3			4.8	0.2		
2	0.9	85		10								
3	8.0	90		5	4.7			0.3				
4	4.0	70		10	4				1		4	11
5	2.2	75	4	10	3				2		6	
7	10.0	91			6						3	
2	9.0	76		9	7		3.0			0.95	4.05	
4	5.0	78	5	11							6	
1	5.4	86			7						7	
2	2.1	70	5	5	5	0.1	0.2	4.6	5	0.1	5	
7	2.0	90		10								
6	2	88			2			10				
3	5	78			5			12			5	
5	8	70	2		8			15			5	
2	10	80						8			12	
1	10	80		10								

CLAIMS

1. A compound of Formula (1):



Formula (1)

wherein:

- A is N, C-Cl, C-CN or C-NO₂;
 L¹ is -OR³;
 Z is -O-, -S- or -NR²-;
 R¹ and R² are each independently H or optionally substituted alkyl;
 R³ is H or alkyl;
 each W independently is -CO₂Q or -SO₃Q;
 each X independently is an optionally substituted amino group or a group which is substituted by an optionally substituted amino group;
 each Y independently is a substituent other than those defined for W and X;
 each Q independently is ammonium or substituted ammonium;
 m, n and p each independently have a value of from 0 to 3; and
 (m+n+p) has a value of from 0 to 5.

2. A compound according to claim 1 wherein each Y independently is halo, hydroxy, nitro, cyano, C₁₋₄-alkyl, C₁₋₄-alkoxy, -SR^a, -COR^a, -COOR^a, -SO₃R^a, -SO₂R^a or -SOR^a; wherein R^a is optionally substituted C₁₋₄-alkyl; wherein the optional substituents are selected from carboxy, sulpho, hydroxy, nitro, cyano and halo.

3. A compound according to any one of the preceding claims wherein the optionally substituted amino groups referred to in the definition of X are of the formula -NR⁴R⁵ wherein R⁴ and R⁵ are each independently H or optionally substituted alkyl; or R⁴ and R⁵ together with the nitrogen atom to which they are attached form a 5- or 6- membered ring.

4. A compound according to any one of the preceding claims wherein:

A is N;

m is 0, 1 or 2;

n is 0 or 1;

p is 0 or 1;

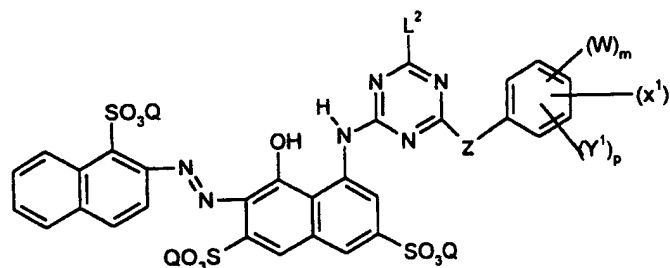
X is of the formula $-NR^4R^5$ or a group which is substituted by $-NR^4R^5$;

Y is halo, hydroxy, cyano, C_{1-4} -alkyl, C_{1-4} -alkoxy, $-SR^a$, $-COR^a$, $-COOR^a$, $-SO_3R^a$, $-SO_2R^a$ or $-SOR^a$;

R^4 and R^5 are each independently H or optionally substituted alkyl, or R^4 and R^5 together with the nitrogen atom to which they are attached form a 5- or 6-membered ring; and

R^a is as defined in claim 2.

5. A compound according to any one of the preceding claims of the Formula (3):



Formula (3)

wherein:

Z is $-O-$, $-S-$ or $-NR^8-$;

R^8 is H or C_{1-4} -alkyl optionally substituted by hydroxy, carboxy, sulphonyl or cyano;

L^2 is $-OR^9$;

R^9 is H or C_{1-4} -alkyl;

each W independently is $-CO_2Q$ or $-SO_3Q$;

each X^1 is $-NR^4R^5$, $-SO_2-NR^4R^5$, $-SO_2(C_{1-10}\text{-alkylene})-NR^4R^5$ or C_{1-6} -alkyl substituted by $-NR^4R^5$;

each Y^1 independently is Cl, nitro, cyano, C_{1-10} -alkyl, or C_{1-10} -alkyl substituted by hydroxy, carboxy, sulphonyl, or C_{1-6} -alkoxy;

Q is ammonium or substituted ammonium;

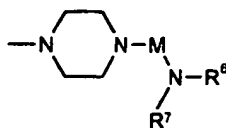
m, n and p are each independently 0 or 1;

$(m+n+p)$ is 1, 2 or 3; and

R^4 and R^5 are as defined in claim 4;

provided that n is 1 when m is 0.

6. A compound according to claim 4 or 5 wherein $-NR^4R^5$ is of the Formula (2):



Formula (2)

wherein:

M is an alkylene linking group; and

R^6 and R^7 are each independently H, C_{1-6} -alkyl or C_{1-6} -alkyl substituted by hydroxy, carboxy, sulpho, amino or C_{1-4} -alkoxy.

7. An ink comprising:

(a) from 0.01 to 30 parts of a compound according to any one of claims 1 to 6 except that Q is any cation; and

(b) from 70 to 99.99 parts of a medium comprising component (i), (ii) or (iii):

(i) a mixture of water and an organic solvent;

(ii) an organic solvent free from water; or

(iii) a low melting point solid;

wherein all parts are by weight and the number of parts of (a)+(b)=100.

8. An ink according to claim 7 wherein Q is sodium, ammonium or substituted ammonium.

9. A process for printing an image on a substrate comprising applying an ink according to claim 7 or 8 to the substrate by means of an ink jet printer.

10. A paper, an overhead projector slide or a textile material printed with an ink according to claim 7 or 8 or by means of a process according to claim 9.

11. An ink jet printer cartridge containing an ink according to claims 7 or 8.

INTERNATIONAL SEARCH REPORT

Int. Application No
PCT/GB 98/01853

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09B43/16 C09D11/02 D06P5/00 //C09B62/245

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09B C09D D06P

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 559 310 A (ZENECA LTD) 8 September 1993 see claims 1-7; example 12 ---	1-11
A	EP 0 481 449 A (SUMITOMO CHEMICAL CO ;TAOKA CHEMICAL CO LTD (JP)) 22 April 1992 see page 16, line 44 - line 51; claim 1 ---	1-11
A	GB 2 171 714 A (RICOH KK) 3 September 1986 see Dye No.12; claims ---	1-11
A	DE 20 62 163 A (KAO SOAP CO., LTD) 24 June 1971 see formulae 31, 34 -----	1-6

☐

Further documents are listed in the continuation of box C.

☒

Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

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- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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- "&" document member of the same patent family

Date of the actual completion of the international search

8 October 1998

Date of mailing of the international search report

22/10/1998

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 98/01853

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0559310	A	08-09-1993	AT 136324 T	15-04-1996
			AU 3102693 A	09-09-1993
			CA 2087489 A	07-09-1993
			DE 69302039 D	09-05-1996
			DE 69302039 T	12-09-1996
			JP 5311087 A	22-11-1993
			US 5383960 A	24-01-1995
EP 0481449	A	22-04-1992	JP 4285677 A	09-10-1992
			JP 4153272 A	26-05-1992
			DE 69118302 D	02-05-1996
			DE 69118302 T	12-12-1996
			US 5183501 A	02-02-1993
GB 2171714	A	03-09-1986	JP 1888511 C	07-12-1994
			JP 6013653 B	23-02-1994
			JP 61195176 A	29-08-1986
			DE 3606219 A	28-08-1986
			US 4647310 A	03-03-1987
DE 2062163	A	24-06-1971	JP 49026286 B	08-07-1974
			JP 49008005 B	23-02-1974